MINUTES OF THE FORTY-SECOND MEETING OF THE

CCQM GAS ANALYSIS WORKING GROUP

HELD ON THE 23rd SEPTEMBER 2020

VIRTUAL

Paul Brewer (Chair)	NPL
Sangil Lee (Deputy Chair)	KRISS
Damian Smeulders (Rapporteur)	NMIA
Shankar Aggarwal	NPLI
Florencia Almirón	LATU
Cristiane Augusto	INMETRO
Dmitrii Belenky	VNIIFTRI
Jan Beranek	CMI
Alda Botas	IPQ
Angelique Botha	NMISA
Jennifer Carney	NIST
Christina Cecelski	NIST
Andrea Chamorro	INTI
Ian Chubchenko	VNIIM
Andreia de Lima Fioravante	INMETRO
Florbela Dias	IPQ
Volker Ebert	PTB
Tahir Erinç Engin	UME
Teresa Fernández Vicente	CEM
Edgar Flores Jardines	BIPM
Marina Froehlich	BEV
Judit Fuko	BFKH
Holger Gerwig	UBA
Wilma Travnicek	UBA
Bradley Hall	NOAA/ESRL
Kimberley Harris	NIST
Joseph Hodges	NIST
Stefan Horender	METAS
Mudalo Jozela	NMISA
Jinsang Jung	KRISS
Fuu Ming Kai	NMC, A*STAR
Heinrich Kipphardt	BAM
Jorge Koelliker Delgado	CENAM
Ovsiy Levbarg	Ukrmetrteststandard
Tatiana Macé	LNE
Michael Maiwald	BAM
Andreas Nowak	PTB
Narine Oganyan	VNIIFTRI
Maria Mabel Puelles	INTI
Paul Quincey	NPL
Andrés Rojo Esteban	CEM
Francesca Rolle	INRIM
Karri Saarnio	FMI
Michela Sega	INRIM
Takuya Shimosaka	NMIJ/AIST
Ana Inés Silva	LATU
Ratirat Sinweeruthai	NIMT
Daya Soni	NPLI
Abdullah Sulaiman Alowaysi	SASO-NMCC
Christophe Sutour	LNE

Shinji Uehara	CERI
Masaru Yamazawa	CERI
Dai Akima	CERI
Oksana Tarasova	WMO
Tanil Tarhan	UME
Miroslava Valkova	SMU
Adriaan van der Veen	VSL
Janneke van Wijk	VSL
Joële Viallon	BIPM
Olav Werhahn	PTB
Robert Wielgosz	BIPM
Dave Worton	NPL
Tiqiang Zhang	NIM
Zeyi Zhou	NIM

1. WELCOME ADDRESS

Paul Brewer gave a welcome address to open the 42nd meeting of the CCQM-GAWG. Paul thanked several participants including:

- Jennifer Carney for representing the GAWG on the KCWG
- Adriaan van der Veen for representing the GAWG at a new CCQM strategy task group, to develop the terms of reference for a new ad-hoc working group that will revise and update CCQM/13-22
- Damian Smeulders for acting as rapporteur
- Sangil Lee for his role as Vice Chair

2. KEY COMPARISONS

Overview of current CCQM-GAWG key comparisons

Paul Brewer presented the current list of key comparisons. He highlighted:

- One comparison is at the Draft B stage CCQM-K41.2017 (hydrogen sulphide in nitrogen)
- Comparisons at the Draft A stage that will be discussed in individual meetings:
    - CCQM-K150 and P189 on particles
    - CCQM-K10.2018 on BTEX
    - CCQM-K117 on ammonia
    - CCQM-K74.2018 on nitrogen dioxide
    - CCQM-K118 on natural gas
- Other studies where work is in progress includes:
    - CCQM-P172 on nitric acid
    - CCQM-K68.2019 and P206 on nitrous oxide
    - CCQM-K26b.2019 on sulphur dioxide in air
    - CCQM-K3.2019 on automotive gases
- Comparisons at the planning stage including studies on CCQM-K165 (dimethyl sulphide in nitrogen), CCQM-P204 (C and O isotope ratio in pure carbon dioxide) and CCQM-K164 (hydrogen purity).
- There were 3 key comparisons that were recently approved by the CCQM. These were CCQM-K171 (CO in nitrogen) coordinated by VNIIM, oxygenated VOCs in air coordinated by VSL and HCl in nitrogen coordinated by KRISS. The last two are awaiting comparison numbers.

Paul commented that the KCDB is moving to a new platform. Coordinators of comparisons need to regularly update the status of comparisons in the database.

Comments:

- Oksana Tarasova asked where the key comparison meetings are listed.
- Robert Wielgosz replied that invitations to key comparison meetings are circulated by email and the meetings are also listed in an open access BIPM document.
- Adriaan van der Veen asked if there is a Draft B report available for CCQM-K150.
- Paul replied that the study is not yet at the Draft B stage.

Reporting results - towards a standardised template

Adriaan van der Veen gave a presentation that examined the contents of measurement reports for key comparisons. He stated that the reporting requirements are clear and are described in the CIPM guidelines.

Adriaan said that measurement results should be reported within 6 weeks in the format detailed in the study protocol along with a complete measurement uncertainty budget. He said it is common that not all datasets are consistent and if the measurement report only provides a glimpse of what is done then it is not possible to scrutinise the results. He said often there are no details provided to support the uncertainty budget.

Adriaan commented that the CMC review relies heavily on the measurement report to support CMCs. He said measurement reports must contain the following:

- The reported value, measurement uncertainty and coverage factor
- A clear definition of the measurand
- The measurement model
- Input quantities
- The mechanism for propagating measurement uncertainty
- Intermediate results

Adriaan stated that accepted symbols should be used, and the measurement equations are to be traceable. He said the report should be written to support the stated uncertainty.

Planning - protocol and HFTLS statement for GAWG approval

CCQM-Kxxx: HCl in N_2

Jinsang Jung presented the plans for a key comparison on hydrochloric acid in nitrogen. He described the development of 100 µmol mol^{-1} HCl PRMs at KRISS with work focussing on minimising the loss of HCl in the cylinder and on wetted components including regulators. Studies at KRISS have determined that nickel coated parts are better for stability (rather than stainless steel) with mixtures being stable for periods of > 7 months at 100 µmol mol^{-1}. Jinsang reported that current work is focussing on developing mixtures at 30 µmol mol^{-1}. Jinsang said that NDIR is used for the measurement of HCl as the instrument consumes only a small amount of gas and is reproducible.

Jinsang described the plans for the key comparison:

- The comparison will be delivered at 30 µmol mol^{-1} HCl in nitrogen
- Mixtures will be made by gravimetry at KRISS
- The HFTLS will cover mixtures over the range 15-100 µmol mol^{-1}

The schedule for the comparison was presented as:

April 2021: Agreement on protocol
June 2021: Shipment of cylinders to participants
November 2021: Reanalysis and stability monitoring at KRISS
February 2022: Draft A report released to participants

Comments:

- Paul Brewer asked if there is a study number for the comparison.
- Jinsang Jung replied that there was no number.
- Paul Brewer indicated that he will provide the form to register the study to KRISS.
- Robert Wielgosz asked if the gravimetric value is a reliable reference value for the comparison or if it drifts over time.
- Jinsang Jung replied that KRISS have published a paper on the work on HCl with the amount fractions independently validated using ion chromatography.
- Robert Wielgosz asked for details of the decay function over time.
- Jinsang said that the long-term stability had been monitored for 2 years in aluminium cylinders.
- Robert Wielgosz asked if the measurements had been made against fresh standards to monitor the stability.
- Jinsang said that new and old cylinders had been compared.
- Paul Brewer commented that the HFTLS range will be discussed off-line as there were concerns the range was too narrow.

Action: Jinsang Jung to obtain a CCQM study number for the comparison and prepare the protocol for GAWG approval (April 2021).

CCQM-Kxxx: Oxygenated VOCs

Adriaan van der Veen presented a proposal for a key comparison on trace level VOC oxygenated components due to their key role in atmospheric chemistry and the need for traceable standards for the WMO-GAW network.

Adriaan commented that VSL had been working with standards containing acetone, ethanol, and methanol at 5 µmol mol^{-1} and 100 nmol mol^{-1}. He said the proposal for the comparison is to provide gravimetric mixtures in the

100 – 200 nmol mol^{-1} range in a matrix of nitrogen. However, as there are substantial cylinder wall interactions the reference values will be assigned against values from permeation systems. Adriaan said that the comparison should also provide support for some other related oxygenated components.

A proposed timeline for the comparison was presented as:

October 2021: Mixtures distributed to participants
February 2022: Measurement reports submitted
April 2022: Preliminary results available to participants

Action: Adriaan van der Veen to obtain a CCQM study number for the comparison and prepare the protocol for GAWG approval.

CCQM-K171: CO in N_2

Ian Chubchenko presented a proposal for a Track A comparison on carbon monoxide at 100 µmol mol^{-1} in nitrogen. The comparison will operate using model 2, where participants ship a cylinder to VNIIM for measurement to assess their preparative capabilities. Ian reported that the KCRV will be determined from a regression of the largest consistent set of standards. Measurements at VNIIM will be made on a Teledyne T300 CO analyser and by GC-FID.

The proposed HFTLS is to cover carbon monoxide in nitrogen or air from the smallest expanded uncertainty to 500 mmol mol^{-1}. It will also provide evidence for those that use the flexible scheme.

Proposed timetable for comparison:

October 2020: Draft protocol
Q4 2022: Mixture preparation
Q2 2023: Shipment of mixtures to VNIIM
Q3-Q4 2023: Measurements at VNIIM
Q1-Q2 2023: Long term stability monitoring by participants
Q3 2023: Draft A report

Participants: restricted to three NMIs per RMO
VNIIM, IPQ, VSL, KRISS, UME, SMU, NMISA, BAM, NPL, BFKH, INMETRO, NPLI, NMIA, PTB, CENAM, LNE, CERI/NIMJ and Ukrmetrtertstandart would all like to participate.

Comments:

- Robert Wielgosz asked if any labs without preparative capabilities would participate.
- PTB would like to participate but do not have a preparative capability.
- Adriaan van der Veen said a model 2 comparison requires less resources and said the model could be used for dissemination to the RMOs

Action: Ian to identify participants for the key comparison and prepare the protocol for GAWG approval.

CCQM- GAWG strategic plan

Paul Brewer presented the list of future comparisons for the GAWG. Analysis has been performed looking at the institutes that have delivered comparisons in the past and identified those institutes with the capability to deliver future comparisons.

Comments:

- Robert Wielgosz commented that at the April 2021 meeting the future plans of the BIPM including the delivery of future key comparisons will be discussed.

Action: All GAWG members to review the comparison plan and provide input where required.

CCQM-K3.2019 (HFTLS statement and track A guidance)

Adriaan van der Veen provided an update on the current key comparison on automotive exhaust. At the time of the meeting results had been received from four participants and it was anticipated that the Draft A report would be available in April 2021.

Adriaan reported that in the protocol the HFTLS had the following upper and lower limits:

- Carbon monoxide 0.1 – 8 %mol/mol
- Carbon dioxide 1-17 %mol/mol

- Propane: 10-5000 µmol/mol
- Oxygen: 0.1-22 %mol/mol

As the study is a Track A comparison, he asked how we should apply the results in the flexible CMC scheme. Adriaan proposed that a pooled relative uncertainty from the four components be used. All GAWG members were in agreement.

3. PROGRESS REPORTS FROM THE REGIONAL METROLOGY ORGANISATIONS

APMP

Takuya Shimosaka provided the progress report for the APMP region. The following comparisons were active:

- APMP.QM-S12 has been finalised (BTEX)
- APMP.QM-S13 and APMP.QM-S14: are at the Draft A (N_2O and HAPs)
- APMP.QM-S18: SO_2 comparison has been delayed due to issues with shipping and COVID-19
- APMP.QM-S7.1: CH_4 results were presented
- APMP.QM-S15: CO_2 results presented. All results agree with KCRV
- APMP.QM-S9 under review (CO in nitrogen)
- APMP.QM-K90 formaldehyde at 2 µmol mol^{-1}, cylinders will be distributed in 2021

Shimosaka reported that this year the APMP TCQM meeting will be held in November by video conferencing. The meetings of the APMP Gas analysis working group and the Focus group on climate change and clean air have both been cancelled.

Comments*:*

- Adriaan van der Veen asked how the RMO comparison on formaldehyde is linked to the key comparison. He said that he is interested in the linkages for the supplementary comparisons to the CCQM studies.
- Shimosaka said that the studies are to meet the needs of developing NMIs that cannot participate in the CCQM studies. He said there has been no discussion on how the studies are linked to the KCs. He said supplementary comparisons are not necessarily linked to the key comparisons.
- Robert Wielgosz said the regional comparisons should be linked to the CC comparisons, with comparable HFTLS statements for the comparisons.

COOMET

Olga Efremova presented current activities in COOMET where there is one active comparison:

- COOMET.QM-K120 CO2 in air. Participants provided two cylinders at 480 and 800 µmol mol^{-1}

The air matrix had to be the same as in the key comparison. The cylinders are currently being shipped to VNIIM for measurement.

- Planned comparison linked to CCQM-K118 on hydrogen enriched natural gas is planned to start in 2022

EURAMET

Janneke van Wijk presented the activities in the EURAMET region where there are five active projects:

- Euramet708: bilateral comparisons between NIST and VSL
- Euramet1305: bilateral comparisons between NPL and VSL
- Euramet1435: Pilot study on aerosol particle number concentration
- Euramet1480: Pilot comparison for particle number concentration up to 500000 cm^{-1} (just started)
- Euramet.QM-K3.2018: comparison on automotive gas mixtures
- A new bilateral comparison has been proposed between PTB and KRISS on HCl in nitrogen

Janneke commented that 18 institutes submitted a total of 185 CMCs for review in the cycle.

SIM

Andreia de Lima Fioravante reported on activities in the SIM region where there are three active comparisons:

- SIM.QM-S9 Biogas. Contains 5 components and a higher oxygen level than in the key comparison. Participants: INMETRO, INTI, CENAM, IBMETRO. Cylinder distribution planned for October 2020.

- SIM.QM-S6: automotive emissions. Participants: INMETRO, INTI, CENAM, IBMETRO, LATU, INACAL. November 2020 despatch.
- SIM.QM-S5: Natural gas. CENAM is the pilot lab. Study is close to completion.

4. TASK GROUPS

Purity Analysis

Sangil Lee reported on the guidance document for CMC claims for purity. The document has sections on:

- How we perform purity analysis and the evidence to support metrological traceability and CMCs
- Primary methods used in the working group
- Purity analysis and ISO 19229

Sangil reported that the summary examines the measurement of significant and insignificant impurities in pure gases and how metrological traceability is realised. He said that the results of the purity analysis are captured in the key comparison measurement reports which can be used as evidence for traceability and for CMC claims. Sangil commented that the document explains how reference gases are manufactured and the role of purity analysis. The document also includes examples from key comparison were the purity analysis impacts on the final report and the measurement uncertainties. A table has been included in the document examining the approaches to purity measurement in the different working groups.

Comment:

Paul Brewer said that the document will be circulated to the working group once the task group has approved the document.

Action: Sangil Lee to finalise document with the task group members and circulate to the GAWG.

Coordinating key comparisons

Paul Brewer reported that a task group was formed at the last meeting at METAS to examine the coordination of key comparisons. A graph was presented showing the labs that have coordinated key comparisons which indicates that a small number of organisations have delivered the majority of the comparisons. Paul reported that a document has been developed on how to deliver comparisons (GAWG 20/02) with the goal of sharing the responsibility by developing the skills needed to deliver comparisons.

Paul commented that a table will be populated for the delivery of future comparisons.

Action: All GAWG members to provide input to the capability spreadsheet .for future coordination of key comparisons and pilot studies.

Proposal for a task group on advanced spectroscopy

Joseph Hodges presented a proposal for a new task group examining the use of quantitative spectroscopy to measure composition and isotopic composition without reference materials. He said the vision is to bring together the expertise in metrology and molecular spectroscopy to allow accurate determination of amount of substance. Joseph said that it is likely to develop 2 types of studies looking at spectroscopic equivalence, and absolute line intensities. Joseph asked for interested people to contact him. There was interest expressed by PTB, KRISS and VSL.

Action: Joseph Hodges to draft the terms of reference for the new task group.

5. PROGRESS ON THE REVIEW OF CMCS

CMC review

Jennifer Carney reported on the review of CMCs in the current cycle. She reported that there had been a total of 1456 CMCs submitted this cycle. In the gas area there were 83 new CMCs and 491 revised CMCs submitted, plus 89 CMCs deleted (663 total).

Jennifer reported that there will be no rereview this cycle as we transition to KCDB 2.0. To utilise the new database a Login is required for CMC writers, reviewers, TC chairs, WG chairs, and KCWG chairs. She said that there are instructional videos provided for the new platform.

Jennifer reported on the special issues from this cycle:

- NMIs reported overlapping values in claims. The claims were mostly accepted but could be discussed further in the working group.
- Sorption tubes: Do the tubes belong in Category 4? What should be the analyte, matrix, amount and units, and can GAWG practices be adapted to these new and different things.
- Is the GAWG strategy document too restrictive, and is further guidance needed when there are improvements over time leading to a decrease in the claimed measurement uncertainty.

6. UPDATES FROM INTERNATIONAL ORGANISATIONS / ACTIVITIES

BIPM Gas Metrology Comparison Programme

Robert Wielgosz discussed the 2020-23 work programme at the BIPM and listed the 7 comparisons in the current period.

BIPM.QM-K1: On-going ozone comparison. During 2020, comparisons were completed with ECCC (Canada) and METAS. A comparison with INRIM is planned for late 2020. The electronics upgrade project is continuing but is waiting on the development of new software. An Ozone workshop along with a survey on the implementation of the new cross section will take place in October 2020.

CCQM-K74.2018: Nitrogen dioxide. The project allowed the examination of the decay of NO_2 standards and the development of 6 different models. The decay rate does not appear to be linear as assumed during the development of the key comparison protocol.

CCQM-P172: Looking at nitric acid in NO_2 mixtures. CENAM, VSL and NPL provided mixtures for the comparison.

CCQM-K120: Key comparison on carbon dioxide in air was completed. The manometric system (PVT) work has continued and should be completely validated by February 2022. The manometric system offers the advantage that a reference value can be provided at any time. Performance of the system at 2 levels (590 and 735 µmol mol^{-1}) were displayed showing very good reproducibility.

CCQM-P204: Accounting for CO_2 isotope ratio variations. Study includes 14 participants (10 NMIs, 4 expert labs). Small cylinders are being delivered and filled by the BIPM. The gas will be distributed in February 2021 in conjunction with the IAEA who will measure the reference values of each batch.

CCQM-K68 on N_2O. All measurements at the BIPM have been completed. Results are due by the end of 2020.

Training programme using FTIR for gas analysis has been a casualty of COVID. Only 2 visiting scientists attended the BIPM in 2020. No visiting scientists are planned for 2021. The visiting scientist programme will be replaced with an e-learning programme.

Work with METAS on dynamic gas standards is continuing and an instrument will be shared. E-learning will be delivered in the area.

Robert reported that the 2024-27 BIPM work programme will be developed next year.

Activities in ISO/TC158

Adriaan van der Veen provided an update on activities at ISO/TC158. He reported that recently completed projects include:

ISO 6141:2015/Amd1
ISO 6145 Gas analysis - Preparation of calibration gas mixtures using dynamic methods - Part 1: Methods of calibration

Work in progress includes:

ISO 14912 conversion of gas mixture composition data
ISO 6142-2 Class 2 mixtures
ISO 19230 (sampling guidelines)
ISO 6142-1 amendment to formulas.
ISO 12963 amendment to formula 5

Adriaan said that there are several new topics being considered at the meetings including:

- isotopic composition of gases
- Impacts on standard atomic weights
- Commutability of analysers
- Reference atomic weights for gas analysers

Adriaan extended an invitation to join the technical committee through national standardisation bodies.

International coordination of aerosol analysis activities

Stefan Horender (METAS) discussed activities on aerosol analysis. He said that Switzerland was the first country to introduce PNC (particle number concentration) to detect faulty diesel particle filters leading to a need for traceable reference instruments to measure these parameters and to the EURAMET comparison (1480). The comparison looked at the comparability of instruments as they measure the soot from the METAS soot generator. The results of the comparison will be reported in 2021 and will feed into the future strategy of the working group examining particles.

7. CCQM-GAWG STRATEGY DOCUMENT

Paul Brewer commented that a survey to gauge the interest and motivations of the different institutes had been distributed. A task group is being formed and their first task will be to create the first draft of the strategy. The draft document will be circulated to the task group using an online platform. It will then be circulated to the working group to seek input and changes.

Action: Paul Brewer to circulate the results of the survey and GAWG 2021-2030 strategy for comment.

8. NEXT MEETINGS AND OTHER ANNOUNCEMENTS

- 43rd GAWG meeting: likely to be virtual (26-27 April 2021)
- 44th GAWG meeting: venue to be confirmed (November 2021)
- EGU: Vienna (25-30 April 2021)
- Gas Analysis Symposium: The Hague (22-24 June 2021). Call for abstracts is open and there will be a session on gas metrology.

END OF MEETING